

Studies of Water-in-Oil Emulsions: Stability and Oil Properties

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ABSTRACT

This paper summarizes studies to determine the stability of water-in-oil emulsions resulting from asphaltene or resin content and viscosity stabilization.

These studies have confirmed that the stability of emulsions can be grouped into three categories: stable, unstable and meso-stable. Water can also reside in oil as 'entrained water', in which larger droplets of water are temporarily suspended by viscous forces. These have been distinguished by physical measures as well as visual differences. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at about three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than about 20 times greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. A meso-stable emulsion has properties between stable and unstable, however breaks down after a few days of standing. The usual situation is that emulsions are obviously either stable, meso-stable or unstable. Entrained water, water suspended in oil by viscous forces alone, is also evident. Very few emulsions have questionable stability. Analytical techniques were developed to test these observations.

Studies in the past four years have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several days to years. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of all water-in-oil states resulting from oil/water mixtures prepared in this study, has been performed for at least one week. This shows that meso-stable emulsions, unstable emulsions and entrained water states clearly separate into oil and water layers. Stable emulsions increase in apparent viscosity and elasticity.

The stability of emulsions has been studied by examining the asphaltene and resin content and secondarily, the visco-elastic properties of eighty-two oils. Results are reported which show that these factors are responsible for the stability regimes noted.

1.0 Introduction

The most important characteristic of a water-in-oil emulsion is its "stability". The reason for this importance is that one must first characterize an emulsion as stable (or unstable) before one can characterize the properties. Properties change very

significantly for each type of emulsion. Until recently, emulsion stability has not been defined (Fingas *et al.* 1995). Therefore, studies were difficult because the end points of analysis were not defined. This paper will describe stability of water-in-oil emulsions and define characteristics of different stability classes. Four 'states' that water can exist in oil will be described. These include: stable emulsions, meso-stable emulsions, unstable emulsions (or simply water and oil) and entrained water. These four 'states' are discriminated by visual appearance as well as by rheological measures.

Studies in the past three years have shown that a class of very 'stable' emulsions exists, characterized by their persistence over several months. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for as long as 3 years in the laboratory. 'Unstable' emulsions do not show this viscosity increase and their viscosity is less than about 20 times greater than the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude greater than the starting oil. The present authors have studied emulsions for many years (Bobra *et al.* 1992; Fingas *et al.*, 1993, 1994, 1995, 1996, 1997). The last three of these references describes studies to define stability. The findings of these studies are summarized here. It was concluded both on the basis of the literature and experimental evidence above, that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in apparent viscosity with time (ie. their elasticity increases). The stability derives from the strong visco-elastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas *et al.* 1995). It was suspected that mesostable emulsions lack sufficient asphaltenes to render them completely stable or still contain too many de-stabilizing materials such as smaller aromatics. Further light is shed on their stability in this paper. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be red in appearance or black. Mesostable emulsions are probably the most commonly-formed emulsions in the field.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water (usually less than about 10%) may be retained by the oil, especially if the oil is viscous.

The most important measurements to characterize emulsions are forced oscillation rheometry studies. The presence of significant elasticity clearly defines whether or not a stable emulsion has been formed. The viscosity by itself can be an indicator (not necessarily conclusive, unless one is fully certain of the starting oil viscosity) of the stability of the emulsion. Colour is an indicator, but may not be definitive. This laboratory's experience is that all stable emulsions were reddish. Some meso-emulsions had a reddish colour and unstable emulsions were always the colour of the starting oil. Water content is not an indicator of stability and is error-prone because of 'excess' water that may be present. It should be noted however that stable emulsions have water contents greater than 70% and that unstable emulsions or entrained water-in-oil generally have water contents less than 50%. Water content

after a period of about one week is found to be more reliable than immediate water content. This is because separation will occur in those emulsions that are less stable.

This groups' findings are paralleled by other researchers in the literature. Sjöblom and fellow researchers at the University of Bergen have conducted many studies on emulsions and have defined different stability classes based on dielectric properties (Sjöblom and Førde, 1996; Førde *et al.* 1996a, 1996b; Førde and Sjöblom, 1996; Dukhin and Sjöblom, 1996). This group has also noted that more stable emulsions result from higher asphaltene contents and that resins appear to make less stable emulsions than do asphaltenes. Several recent papers have reported on results confirming that asphaltenes are largely responsible for emulsion stability (do Carmo Marques *et al.* 1997; Friberg and Yang, 1996; McLean and Kilpatrick, 1997a, 1997b; Neumann and Paczynska-Lahme, 1996; Puskas *et al.* 1996). The role of resins has been assigned as secondary, but essential. The consensus of the literature is as follows:

1. stable and less-stable emulsions exist,
2. emulsion stability results from the viscoelastic films formed by asphaltenes at the oil-water interface,
3. asphaltenes produce more rigid films than do resins,
4. stable emulsions might be classified by their dielectric and viscoelastic properties,
5. water content does not appear to correlate direct with stability, however, very low or very high water contents (<50 or >90%) are not correlated with stable emulsions,
6. most researchers use visible phase separation to classify emulsions as stable or not and most concede that this is not an optimal technique.

3.0 Experimental

Water-in-oil emulsions were made in a rotary agitator and then the rheometric characteristics of these emulsions studied over time. Eighty-two oils were used. Oils were taken from the storage facilities at the Emergencies Science Division. Properties of these oils are given in standard references and will be summarized later in this paper (Jokuty *et al.* 1996).

Emulsion Formation - Emulsions were made in an end-over-end rotary mixer (Associated Design). The apparatus was located in a temperature controlled cold room at a constant 15 degrees Celsius. The mixing vessels were 2.2 L FLPE wide-mouthed bottles (Nalge). The mixing vessels were approximately one-quarter full, with 600 mL salt water (3.3% w/v NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted into the rotary mixer, and allowed to stand for several hours (usually three) to thermally equilibrate. The vessels were then rotated for a period of 12 hours at a rate of 55 RPM. The vessels are approximately 20 cm in height, providing a radius of rotation of about 10 cm. The resulting emulsions were then collected into Fleaker jars, covered, and stored in the same 15 degree cold room. Analysis was performed on the day of collection, and again one week later.

Rheology - The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35 mm and 60 mm parallel plates with corresponding base plates,

clean air supply at 40 p.s.i., and a circulating bath maintained at 15.0 degrees Celsius. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a teflon spatula. This was left for 15 minutes to thermally equilibrate at 15 degrees Celsius.

Forced Oscillation - A stress sweep at a frequency of 1 reciprocal second was performed first to determine the linear viscoelastic range (stress independent region) for frequency analysis. This also provides values for the complex modulus, the elasticity and viscosity moduli, the low shear dynamic viscosity, and the $\tan(\delta)$ value. A frequency sweep was then performed at a stress value within the linear viscoelastic range, ranging from 0.04 to 40 Hz. This provides the data for analysis to determine the constants of the Ostwald-de-Waele equation for the emulsion.

Viscosities - The apparent dynamic viscosity was determined on the plate-plate apparatus as well, and corrected for their non-Newtonian behaviour using the Weissenberg equation. A shear rate of 1 reciprocal second was employed for a period of one minute, without ramping.

Water Content - A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 Methanol:Chloroform:Toluene. The specific method used was as follows: standardize the titre and blank the solvent. Stir the sample emulsion to get a relatively homogeneous mixture. Fill a 1 mL plastic syringe with emulsion, trying to avoid free water pockets present in the sample. Eject all but 0.1 mL; this should remove most of the free water from the more viscous emulsion. Weigh the sample syringe and inject into the reaction vessel, being careful the sample goes into the solution and not onto the vessel walls. Reweigh the syringe and enter the difference into the titrator. Initiate titration. Weight percentage of water is displayed.

4.0 Results and Discussion

The rheological data are given in Table 1. The second column of the table is the evaporation state of the oil in mass percent lost. The third column is the assessment of the stability of the emulsion based on both visual appearance and rheological properties. The power law constants, k and n , are given next. These are parameters from the Ostwald de Waele equation which describes the Newtonian (or non-Newtonian) characteristics of the material. The viscosity of the emulsion is next and in column 7, the complex modulus which is the vector sum of the viscosity and elasticity. Column 8 lists the elasticity modulus and column 9, the viscosity modulus. In column 10, the isolated, low-shear viscosity is given. This is the viscosity of emulsion at very low shear rate. In column 9 the $\tan \delta$, the ratio of the viscosity to the elasticity component, is given. Finally, the water content of the emulsion is presented.

Observations were made on the appearance of the emulsions and were used to classify the emulsions. All of the stable emulsions appeared to be stable and remained intact over seven days in the laboratory. All of the meso-stable emulsions broke after a few days into water, free oil and emulsion. The time for these emulsions to break down varies from about 1 to 3 days. The emulsion portion of these break-down emulsions appears to be somewhat stable, although separate studies on this portion has not been performed because of the difficulty in separating these portions from the oil and water. All entrained water appeared to have larger suspended water

droplets. The appearance of non-stable water in oil was just that, the oil appeared to be unchanged and a water layer was clearly visible.

Table 2 provides the data on the oil properties as well as a new parameter called 'stability' which is the complex modulus divided by the viscosity of the starting oil. It is noted from this table that this parameter correlates quite well with the assigned behaviour of the oils. High stability parameters imply stable emulsions and low ones imply unstable emulsions.

The 'stability' parameter was used to study the correlations between the properties of the oil and the stability of the resulting emulsion. The correlations are summarized in Table 3 which shows the regression coefficient (r^2) correlations of stability with the starting oil properties. The regression coefficients were calculated using the program TableCurve (Jandel Scientific, San Rafael, California). The regression coefficients are taken from the highest consistent value of the simple curves fit to a given set of data. Table 3 shows that the correlations vary with each type of emulsion. For all the emulsions and oil in water situations, none of the parameters correlates well with stability, except for the final water content of the emulsion. This is because the less stable emulsions have little water content. It should also be noted that this is not a starting oil property. For stable emulsions, there is only a slight correlation with density and saturates. For meso-stable emulsions, there is a relatively good correlation with density, viscosity, resins, saturates and aromatics. This may indicate that these emulsions are temporarily stabilized by a combination of viscous forces and resin stabilization. Entrained water stability correlates best with density, aromatics, viscosity, and resin content. This indicates that these may be dominated most by viscous forces. Finally, in the case of unstable emulsions, no parameter correlates well. This appears to confirm the findings that none of the stabilization forces noted are operative.

It is important to recognize that there may be a strong interaction between parameters. To check for this, the program TableCurve 3D (Jandel Scientific, San Rafael, California) was used to correlate 3 parameters simultaneously. Results of this are shown in Table 4. Again, only the consistently highest regression coefficient (r^2) was taken. This table shows that several two-way interactions exist. For all water-in-oil forms, there is no significant correlation between the parameters tested. For stable emulsions, there is a strong correlation between stability and viscosity and asphaltenes. This did not show on a two-way parameter correlation, presumably because of the interaction between parameters. The correlation is also illustrated in Figure 1. The best correlation for meso-stable emulsions is that of stability with resins and viscosity, followed very closely by correlations of stability, viscosity with asphaltenes, aromatics and density. The correlation of stability with viscosity and resins for mesostable emulsions is illustrated in Figure 2. The stability of entrained water correlates best with aromatics and density. This correlation is illustrated in Figure 3. Similarly, unstable emulsion 'stability' correlates highly with aromatics and density along with the viscosity. The correlation of unstable emulsions is illustrated in Figure 4.

In all four figures, sharply-defined regions of stability are noted. It is also noted that different forces are evident on the basis of these correlations. For stable emulsions there appears to be a region where viscosity, asphaltenes and resins interact to form a stable emulsion. This is similar in meso-stable emulsions except

Table 2

Oil Properties and Comparison to the One-Week Emulsion Properties

Starting Oil Properties										Emulsion Rheological Properties - One Week After Formation										
Oil	Visual				Stability*	Complex Elasticity					Viscosity Isolated low- tan Water									
	evap. %	stability	Density	Viscosity		Saturates	Aromatics	Resins	Asphaltenes	Waxes	Power Law Constant	K	n	Viscosity Modulus	Modulus	Modulus	shear viscosity	delta	Content	
Sockeye	0	Stable	0.897	45	48	31	13	8	6	95555.56	0.999E+05	0.0544	6.9E+05	4.3E+06	1.0E+06	3.1E+05	8.8E+04	0.11	86.87	
Point Arguello Light	0	Stable	0.874	22	57	27	9	6	6	37727.27	9.871E+04	0.0581	9.6E+04	8.3E+05	8.2E+05	1.4E+05	2.2E+04	0.17	93.76	
Point Arguello Light	10.19	Stable	0.898	76	54	30	9	8	6	36842.11	4.167E+05	0.0372	2.5E+05	2.8E+06	2.8E+06	3.3E+05	5.2E+04	0.12	87.78	
Arabian Light	0	Stable	0.866	14	51	39	6	3	5	32857.14	3.537E+04	0.0860	2.3E+04	4.8E+05	4.8E+05	4.0E+04	6.9E+04	0.14	86.93	
Arabian Medium	0	Stable	0.878	29	54	32	7	6	6	23448.28	8.828E+04	0.0944	5.5E+04	6.8E+05	7.7E+05	7.9E+04	1.2E+04	0.11	84.36	
Point Arguello Light	19.04	Stable	0.913	183	48	31	12	9	7	19125.68	5.054E+05	0.0539	3.1E+05	3.6E+06	3.8E+06	4.2E+05	7.2E+04	0.13	85.83	
Takula	0	Stable	0.864	110	65	22	8	5	8	10909.09	1.806E+05	0.1371	1.2E+05	1.2E+06	1.2E+06	2.1E+05	3.1E+04	0.15	84.18	
Sockeye	12.50	Stable	0.917	163	44	32	15	9	5	6748.47	1.806E+05	0.1871	2.2E+05	1.1E+06	4.3E+06	4.9E+05	5.0E+04	0.31	74.35	
Arabian Light	12.04	Stable	0.892	33	49	37	8	5	5	6060.61	3.596E+04	0.0957	3.1E+04	2.0E+05	2.0E+05	2.7E+04	4.2E+04	0.13	85.82	
Cook Inlet - Swenson River	39.69	Stable	0.914	152	56	29	7	7		5394.74				8.2E+05	7.4E+05	3.3E+05	5.2E+04	0.43	80.78	
Arabian Light	24.20	Stable	0.911	94	46	39	10	6	5	3829.79	4.091E+04	0.1226	4.3E+04	3.6E+05	3.5E+05	7.3E+04	1.1E+04	0.20	83.62	
Sockeye	22.10	Stable	0.926	628	39	34	15	15	5	2388.54	2.396E+05	0.1948	3.1E+05	1.5E+06	1.4E+06	6.0E+05	7.8E+04	0.35	70.39	
Arabian Medium	13.15	Stable	0.91	91	42	44	7	7	5	2307.69	2.663E+04	0.4521	2.8E+04	2.1E+05	1.8E+05	1.2E+05	1.9E+04	0.84	77.06	
Point Arguello Light	28.33	Stable	0.929	671	45	32	12	11	8	2235.47	1.620E+05	0.1723	1.8E+05	1.5E+06	1.4E+06	4.2E+05	6.8E+04	0.28	75.89	
Point Arguello Comingled	0	Stable	0.925	533	36	25	23	16	8	2063.79	1.493E+05	0.2863	1.8E+05	1.1E+06	1.0E+06	4.1E+05	6.4E+04	0.36	82.19	
Takula	8.31	Stable	0.886	844	62	24	10	4	8	1421.80	1.528E+05	0.1744	1.3E+05	1.2E+06	1.1E+06	2.3E+05	3.6E+04	0.20	77.18	
Hondo	0	Stable	0.938	735	33	31	24	12	4	1197.28	1.665E+05	0.1825	1.7E+05	8.8E+05	8.3E+05	2.5E+05	4.2E+04	0.32	76.96	
Arabian Medium	20.77	Stable	0.926	275	40	46	8	7	5	363.64	1.117E+04	0.8129	2.3E+04	1.0E+05	5.0E+04	9.2E+04	1.5E+04	1.8	72.68	
Point Arguello Heavy	0	Stable	0.945	3250	32	32	17	19	6	221.54	8.787E+04	0.4322	1.8E+05	7.2E+05	6.8E+05	3.9E+05	6.6E+04	0.72	74.87	
Arabian Medium	30.93	Stable	0.95	2155	33	54	9	7	5	185.61	5.757E+04	0.4417	5.4E+04	4.0E+05	3.2E+05	2.2E+05	3.6E+04	0.70	65.60	
Point Arguello Comingled	9.05	Stable	0.953	4988	31	33	19	17	4	124.30	1.651E+05	0.3100	1.5E+05	6.2E+05	4.7E+05	4.3E+05	7.0E+04	0.95	69.41	
Hondo	16.67	Stable	0.967	9583	27	33	29	12	4	87.66	1.537E+05	0.5793	2.8E+05	8.4E+05	6.2E+05	6.1E+05	8.0E+04	0.96	64.23	
North Slope (Southern Pipeline)	29.62	No	0.943	961	42	39	13	7		197.71	NM	NM	1.5E+03	1.9E+05	1.7E+05	7.4E+04	1.2E+04	0.42	24.48	
North Slope (Northern Pipeline)	31.14	No	0.94	748	44	37	12	7		147.06	NM	NM	1.2E+03	1.1E+05	9.4E+04	4.7E+04	7.6E+03	0.50	12.80	
North Slope (Middle Pipeline)	30.54	No	0.942	900	42	38	12	7		122.22	NM	NM	1.4E+03	1.1E+05	1.0E+05	4.8E+04	7.4E+03	0.49	19.67	
Santa Clara	0	No	0.92	304	36	22	29	13	6	95.39	2.125E+03	0.9800	2.6E+03	2.9E+04	1.7E+04	2.4E+04	3.9E+03	1.4	12.75	
Bunker C (Anchorage)	6.41	No	1.005	280000	23	42	20	15	2	1										
Carpenteria	0	No	0.916	164	44	30	17	9	7	1										
Hondo	32.29	No	0.988	449700	27	28	32	13	4	1										
Jet Fuel (Anchorage)	0	No	0.811	2	81	19	0	0	0	1										
Jet Fuel (Anchorage)	52.72	No	0.835	3	80	19	0	0	0	1										
North Slope (Middle Pipeline)	0	No	0.876	16	52	35	9	5	1											
North Slope (Northern Pipeline)	0	No	0.872	14	51	34	9	5	1											
North Slope (Southern Pipeline)	0	No	0.877	18	54	32	8	6	1											
Pitas Point	0	No	0.834	2	80	18	3	0	0	1										
Pitas Point	23.56	No	0.854	2	62	35	0	0	0	1										
Point Arguello Comingled	22.12	No	0.985	2E+06	24	33	21	22	5	1										
Point Arguello Heavy	17.78	No	0.991	5E+06	25	34	21	22	4	1										
Sumatran Heavy	0	No	0.931	13300	46	30	13	8	5	1										
Sumatran Heavy	5.26	No	0.937	17000	45	32	16	8	4	1										
Sumatran Light	0	No	0.86	41480	70	15	6	7	24	1										
Tachina	0	No	0.87	5E+06	74	12	9	4	23	1										
Waxy Light Heavy Blend	0	No	0.931	184	39	35	21	5	4	1										
Cook Inlet - Granite Point	0	No	0.829	4	72	22	5	1	1											
Diesel (Anchorage)	0	No	0.83	3	74	24	1	0	0	1										
Diesel (Anchorage)	37.44	No	0.862	5	75	23	1	0	0	1										
Diesel (Mobile Burn #3)	0	No	0.839	4	76	22	2	0	0	1										
Diesel (Mobile Burn #3)	8.21	No	0.843	5	78	20	2	0	0	1										
Diesel (Mobile Burn #3)	16.32	No	0.846	6	78	20	2	0	0	1										
Doe Cuadras	0	No	0.9	51	48	30	17	6	6	1										
Cook Inlet - Swenson River	0	Meso	0.842	6	85	25	6	5		4500	4.378E+02	0.4120	1.9E+03	2.7E+04	2.2E+04	1.7E+04	2.8E+03	0.80	57.50	
Cook Inlet - Trading Bay	33.30	Meso	0.924	278	51	32	9	8		1905.47	1.361E+05	0.1891	4.3E+04	5.3E+05	4.9E+05	1.5E+05	2.9E+04	0.27	61.43	
Takula	15.88	Meso	0.896	3148	60	25	11	4	8	381.19	1.877E+05	0.1791	1.7E+05	1.2E+06	1.2E+06	2.8E+05	4.4E+04	0.24	60.22	
Carpenteria	14.87	Meso	0.948	3426	31	36	22	11	4	84.65	9.734E+03	0.8845	2.1E+04	2.9E+05	2.6E+05	1.5E+05	2.3E+04	0.57	16.04	
Cook Inlet - Granite Point	45.32	Meso	0.903	4119	62	28	7	3		83.12	7.725E+04	0.1401	8.5E+03	2.8E+05	2.8E+05	7.4E+04	1.2E+04	0.30	57.58	
Carpenteria	10.31	Meso	0.93	755	40	30	19	11	5	47.68	4.815E+03	0.8765	2.3E+04	3.9E+04	3.2E+03	3.6E+04	5.8E+03	12	13.82	
Santa Clara	11.40	Meso	0.948	1859	32	28	27	13	4	40.34	1.087E+05	0.1658	1.5E+04	7.5E+04	2.0E+04	7.3E+04	1.1E+04	3.5	38.72	
Doe Cuadras	11.17	Meso	0.927	187	42	31	20	7	4	24.6	NM	NM	5.3E+02	4.6E+03	1.6E+03	4.2E+03	7.0E+02	3.0	26.49	
Doe Cuadras	20.30	Meso	0.947	741	41	31	19	9	6	22.94	NM	NM	1.8E+03	1.7E+04	3.0E+03	1.3E+04	2.1E+03	4.2	28.72	
Santa Clara	21.63	Meso	0.967	22760	28	32	23	17	5	16.26	5.794E+04	0.8751	9.2E+04	3.7E+06	2.0E+05	3.3E+05	5.0E+04	1.65	40.15	
Beldridge Heavy	0	Meso	0.975	12610	28	39	30	3	1	12.69	2.638E+04	0.6938	5.4E+04	1.6E+05	8.2E+04	1.2E+05	2.2E+04	1.8	27.16	
Beldridge Heavy	2.74	Meso	0.977	17105	29	38	30	4	1	10.52	2.779E+04	0.6374	6.2E+04	1.8E+05	1.0E+05	1.4E+05	2.4E+04	1.4	29.47	
Waxy Light Heavy Blend	19.60	Meso	0.975	17260	30	35	28	6	1	8.37	1.884E+04	0.7088	3.7E+04	1.1E+05	5.3E+04	1.0E+05	1.5E+04	2.1	33.58	
Cook Inlet - Trading Bay	0	Meso	0.86	10	62	25	7	5		1										
Platform Irene	0	Entrained	0.991	7600	26	29	22	22	2	434.21	2.744E+05	0.8255	5.4E+05	3.3E+06			4.0E+05	1.20	34.94	
Point Arguello Comingled	15.19	Entrained	0.969	41860	27	33	21	19	4	19.11	9.211E+04	0.7823	1.8E+05	8.0E+05	3.5E+05	7.0E+05	1.1E+05	2.10		

Table 3 Correlation of Stability with Oil Parameters

Oil Parameter	All Water in Oil		Stable Emulsions		Meso-Stable Emulsions		Entrained Water		Unstable	
	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²
Density	0.05	0.05	0.23	0.23	0.73	0.73	0.99	0.99	0.14	0.14
Viscosity	0.05	0.05	0.4	0.4	0.84	0.84	0.36	0.36	0.16	0.16
Saturates	0.04	0.04	0.16	0.16	0.83	0.83	0.02	0.02	0.11	0.11
Aromatics	0	0	0.04	0.04	0.38	0.38	0.99	0.99	0.2	0.2
Resins	0.04	0.04	0.06	0.06	0.8	0.8	0.69	0.69	0.06	0.06
Asphaltenes	0.02	0.02	0.09	0.09	0.04	0.04	0.43	0.43	0.08	0.08
Waxes	0.05	0.05	0.09	0.09	0.09	0.09	0.25	0.25	0.04	0.04
Water in emulsion	--	0.49								

Table 4

Two-Way Correlation of Stability with Oil Parameters

Oil Parameters	All Water in Oil		Stable Emulsions		Meso-Stable Emulsions		Entrained Water		Unstable	
	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²
Viscosity - Asphaltenes	0.19	0.19	0.83	0.83	0.85	0.85	0.54	0.54	0.45	0.45
Viscosity - Resins	0.19	0.19	0.66	0.66	0.87	0.87	0.08	0.08	0.29	0.29
Viscosity - Aromatics	0	0	0.4	0.4	0.85	0.85	0.99	0.99	0.98	0.98
Viscosity - Density	0.19	0.19	0.4	0.4	0.85	0.85	0.98	0.98	0.97	0.97
Viscosity - Asphaltenes&Resins	0.19	0.19	0.72	0.72	0.86	0.86				

that the importance of asphaltenes and resins are reversed. There is a region defined for entrained water on the basis of aromatic content and density. Similarly for unstable emulsions this is also defined by aromatics and density. This confirms previous findings that stable emulsions are the result of stabilization by asphaltenes and to a secondary extent by viscous retention. Resins are only partially responsible and in-fact if the resin/asphaltene ratio rises, the result appears to be a meso-stable emulsion. Meso-stable emulsions are largely the result of resin and viscosity stabilization. Asphaltenes play a secondary role. It is interesting to note that there is a viscosity 'window' for both stable and meso-stable emulsions. Very high viscosity oils do not appear to make either stable or meso-stable emulsions.

It was noted that a stability index calculated by dividing the complex modulus of the emulsion (or remains) after one week divided by the starting oil viscosity, correlates very well to the assignment of the stability class. The stability parameter was correlated with other parameters that might be used as indicators of stability. The results are shown in Table 5. It can be seen from this table that the correlation varies with the type of emulsion or water-in-oil state considered. For all types, there is only a moderate correlation with the water content. It should be noted that this would be expected since the correlation is with the 7-day old sample, and all but stable emulsions have lost a significant amount of their water. There is also a moderate correlation of the Ostwald de Waele equation parameters, which indicate non-Newtonian behaviour in the case of both stable and unstable emulsions and Newtonian behaviour in the case of the entrained water. The entrained water class shows a high correlation with the low-shear viscosity indicating that these are largely viscosity-stabilized. Given the high correlation of the 'stability' index with the assigned properties of the emulsion, there does not appear to be other rheological parameters which can discriminate to the same extent. This is largely a result of the fact that the other parameters are generally relevant to specific water-in-oil classes and none other than the stability covers all 4 classes.

Ternary diagrams of the aromatic, resin and asphaltene components of the four classes of water-in-oil states discussed here, are shown in Figures 5 to 8. These diagrams show that there is overlapping regions for composition of all four types. Unfortunately, a simple compositional analysis will not discriminate between those oils that form emulsions and those that do not. This again indicates that there is a complex interaction between components and the viscosity (and perhaps density) of the oil.

Table 6 shows the differences in the starting oil properties and the final states after one week. This shows that the factor defined as emulsion stability is capable of discriminating among the various states of water-in-oil studied here. Although there are overlapping ranges, the differences are generally sufficient to act as a single-value discriminator. It is noted that there are different viscosity ranges for the different states. This shows that viscous forces are responsible for part of the stability, but that after viscosity of the starting oil rises to a given point, about 20,000 mPa.s, that meso-stable or stable emulsions are no longer produced. This may also explain two outstanding mysteries, that of why Bunker C generally does not form emulsions and why stable emulsions are not commonly seen in actual spills. Bunker C, especially after a short period of weathering, has viscosity too great to form either stable or meso-stable emulsions. Further, if the viscosity of formation is too great, perhaps the

Table 5

Correlation of Stability with Emulsion Parameters

Emulsion Parameter	All Water in Oil		Stable Emulsions		Meso-Stable Emulsions		Entrained Water		Unstable Water	
	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²	Regression Coefficient	R ²
k (Ostwald de Waele equation)	0.6		0.64		0.17		0.89		nr	
n (Ostwald de Waele equation)	0.64		0.65		0.23		0.82		nr	
Emulsion viscosity	0.66		0.61		0.06		0.94		few data	
Complex modulus	0.21		0.5		0.16		0.96		0.01	
Elasticity modulus	0.14		0.14		0.21		0.17		few data	
Viscosity modulus	0.02		0.23		0.08		0.52		few data	
Low-Shear Viscosity	0.05		0.17		0.09		0.95		few data	
tan Delta (V/E)	0.64		0.56		0.11		0.42		few data	
water content	0.74		0.76		0.51		0.4		0.7	

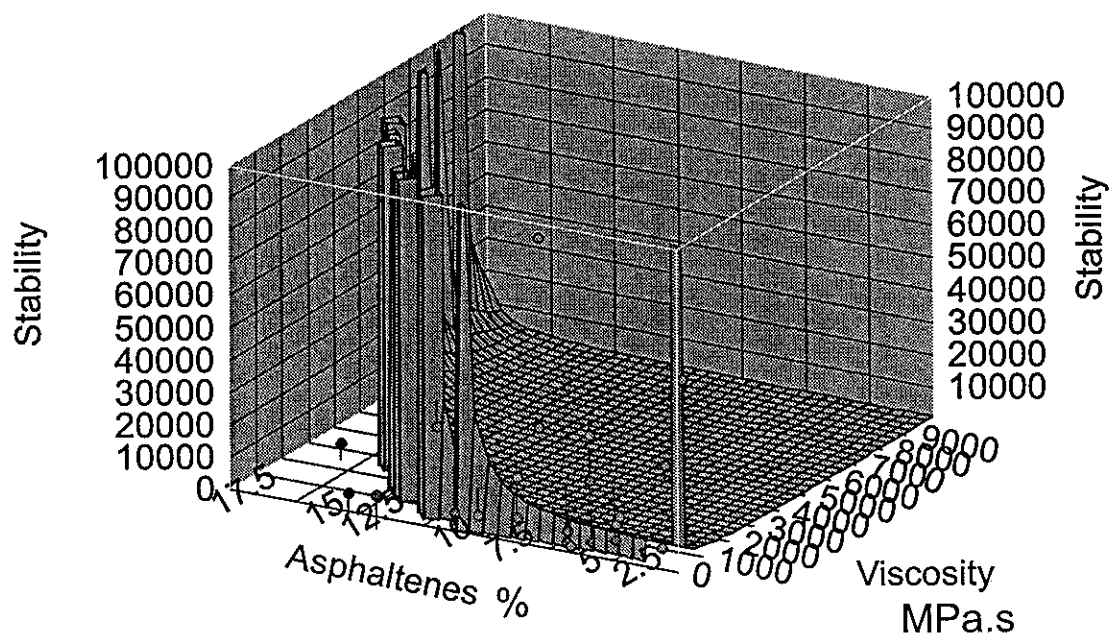


Figure 1 Correlation of Stability with Asphaltenes and Viscosity

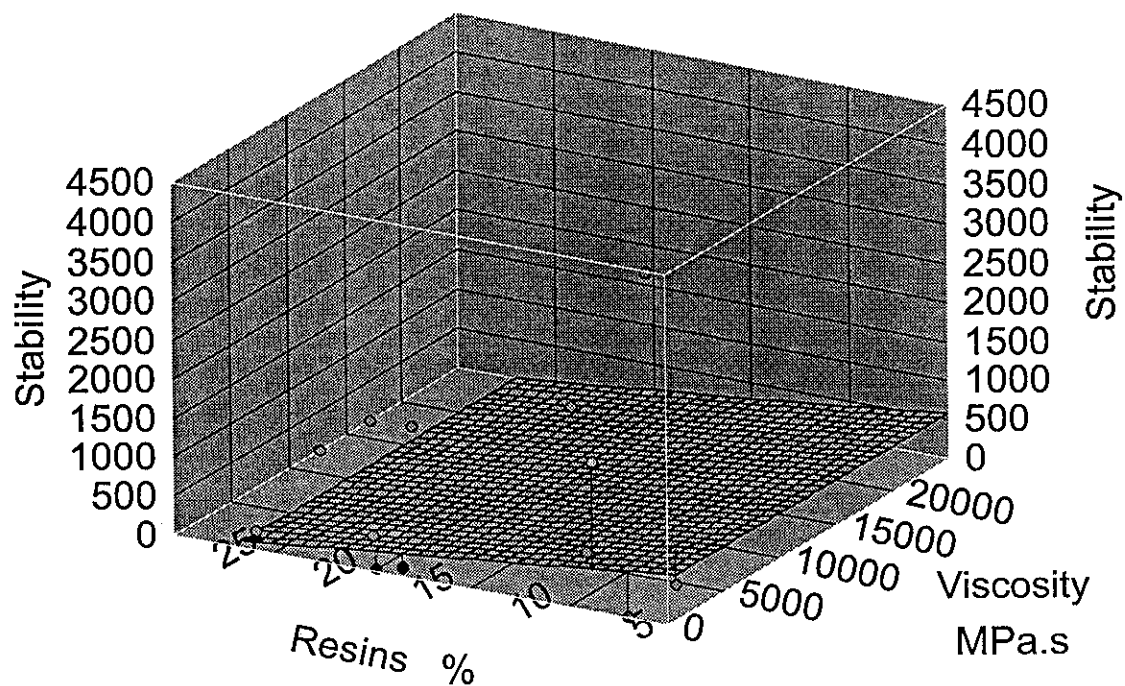


Figure 2 Correlation of Stability with Viscosity and Resins - Meso-stable Emulsions

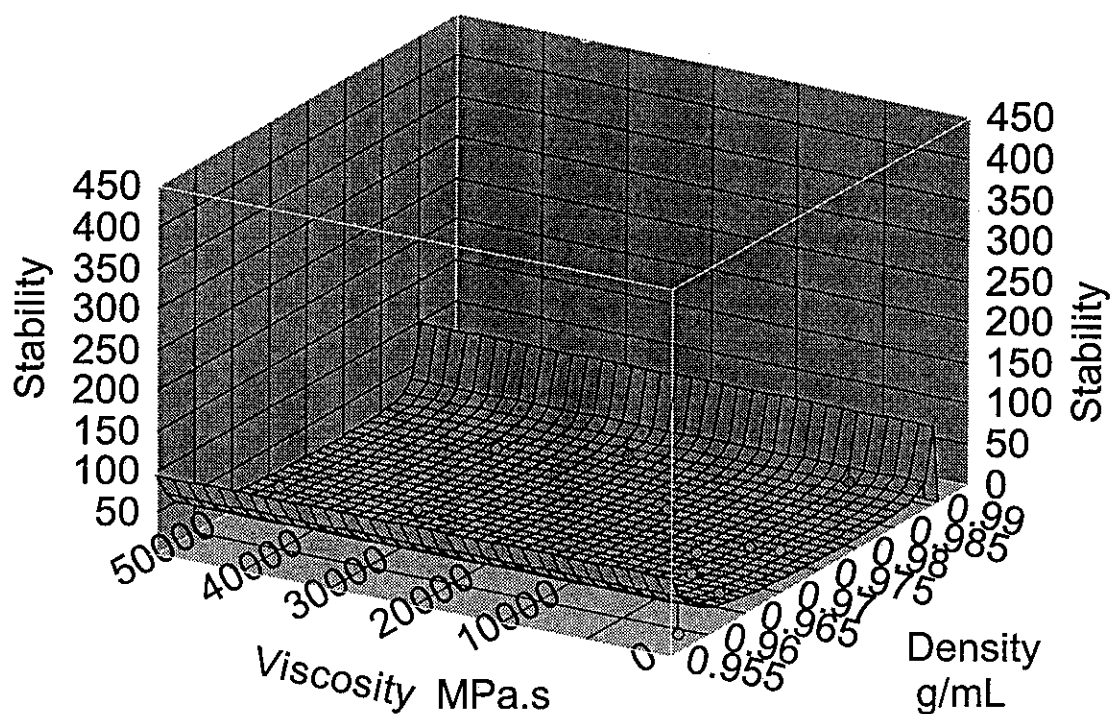


Figure 3 Correlation of Stability with Viscosity and Density - Entrained Water in Oil

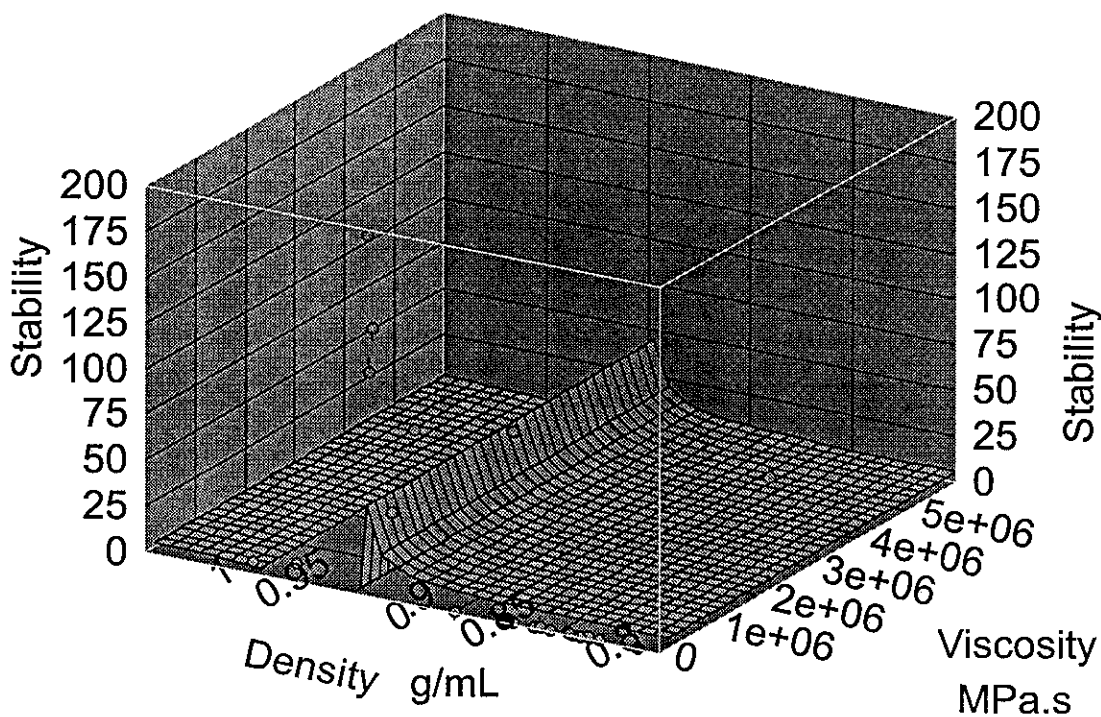


Figure 4 Correlation of Stability with Viscosity and Density - Unstable emulsions

weathering of an emulsion will increase its viscosity past a certain point and then de-stabilization may occur.

Table 6 also shows that the deviation from Newtonian behaviour (as shown by the power law constants) is greatest for the stable emulsions and secondly for meso-stable emulsions and almost no deviation noted for the entrained and unstable cases. This is the result of a high elastic component to the viscosity, as evidenced by the elastic modulus and tan delta for the stable emulsions and slightly for the meso-stable emulsions. The water content, as would be expected, correlates very highly with the state after one week. This is accentuated by the fact that meso-stable and entrained water-in-oil have separated to a significant degree after this time.

Table 7 shows the properties of the water-in-oil states studied here. This shows that the starting oil properties differ somewhat for oils that form the various states. The oil properties for stable and meso stable are similar. These are oils of medium viscosity that contain a significant amount of resins and asphaltenes. Meso-stable emulsions may form from oils that have higher or lower viscosities than those that might form stable emulsions. Stable emulsions are more likely to form from those oils having more asphaltenes than resins. Entrained water is likely to form from more viscous oils with relatively high densities. Oils of very high or very low viscosities (and densities) are unlikely to uptake water in any form. These oils typically have no (associated with low viscosity and density) asphaltenes or resins, or very high amounts of these.

Table 7 also shows that the differences between the four water-in-oil states is readily discernible by appearance and rheological properties. The reddish or brown colour on formation indicates either a stable or meso-stable emulsion, however, stable emulsions always have a more solid appearance. The increase in apparent viscosity (from the starting oil) on formation averages about 1,100 for a stable emulsion, 45 for a meso-stable emulsion, 13 for entrained water-in-oil and unstable show little or no increase. This difference increases after one week. The increase in apparent viscosity after one week averages about 1,500 for a stable emulsion, 30 for a meso-stable emulsion, 3 for entrained water-in-oil and unstable show little or no increase. It is noted that apparent viscosity does not decrease after one-week for stable emulsions only.

There are several other features noted in the summary data presented in Table 7. An examination of the wax content shows that wax content has no relation to the formation of any of these states. There may be some correlation to viscosity but the specific wax content is not associated with the formation of any state. It is noted that density is associated with the viscosity and somewhat to the state. It is also noted that the water content correlates somewhat with the state. The average water content of stable emulsions is 80 % on the day of formation, of meso-stable - 62, of entrained - 42 and 5 for unstable. One must be cautious on using this as a sole discriminator because of over-lapping ranges. The water content after one week, as would be expected, correlates very highly with the state. This, as was noted above, is accentuated by the fact that meso-stable and entrained water-in-oil have separated to a significant degree.

These data indicate that there are 'windows' of composition and viscosity which results in the formation of each of the types of water-in-oil states. The important composition factors are the asphaltene and resin contents. Asphaltenes are

Table 6

Ranges of Properties for the Various Emulsion Stabilities

Emulsion Rheological Properties - One Week After Formation																							
emulsion stability	Property Range	Starting Oil Properties										Waxes						Complex Elasticity				tan delta	Water Content (%)
		Density g/mL	Viscosity mPa.s	Saturates %	Aromatics %	Resins %	Asphaltenes %	%	%	%	%	Power Law Constants	Viscosity Modulus (mPa.s)	Modulus (mPa)	Modulus (mPa)	Viscosity Modulus (mPa.s)	Modulus (mPa)	Modulus (mPa)	Isolated shear viscosity (mPa.s)				
Stable	high	0.9674	9583	65	54	29	19	8	95555.56	8.596E+05	0.8129	6.9E+05	4.3E+06	4.3E+06	6.1E+05	9.0E+04	1.8	93.79					
	low	0.8637	14	27	22	6	3	4	87.66	1.117E+04	0.0372	2.3E+04	1.0E+05	5.0E+04	2.7E+04	1.1E+04	0.11	64.23					
	high difference from unstable	-0.0376	-5128417	-16	12	-3	-3	-16	95357.85	857475	-0.1671	687400	-838000	4130000	536000	78000	0.4	69.31					
	low difference from unstable	0.0527	12	4	10	6	3	4	86.66	11170	0.0372	23000	9998	50000	27000	11000	0.11	64.23					
	high difference from mesostable	-0.0096	-13177	0	15	-1	2	0	93649.09	671600	-0.1636	520000	3100000	3100000	280000	40000	-10.2	32.36					
low difference from mesostable	0.0217	8	-1	-3	0	0	0	3	86.66	10732.4	-0.1029	22470	99990	48400	22800	10300	-0.13	62.34					
Meso	high	0.977	22760	65	39	30	17	8	1906.47	1.877E+05	0.9765	1.7E+05	1.2E+06	1.2E+06	3.3E+05	5.0E+04	12	61.43					
	low	0.842	6	28	25	6	3	1	1	4.376E+02	0.1401	5.3E+02	10	1.6E+03	4.2E+03	7.0E+02	0.24	1.89					
	high difference from unstable	-0.028	-5115240	-16	-3	-2	-5	-16	1708.76	185575	-0.0035	167400	-3938000	1030000	256000	38000	10.6	36.95					
	low difference from unstable	0.031	4	5	13	6	3	1	0	437.6	0.1401	530	8	1600	4200	700	0.24	1.89					
	Entrained	high	0.9907	59390	32	55	31	22	12	434.21	2.744E+05	0.9633	5.4E+05	3.3E+06	6.2E+05	7.0E+05	4.0E+05	9.4	34.94				
low	0.9688	2002	19	29	15	3	1	1	2.763E+03	0.6255	3.7E+03	6400	2.4E+03	1.5E+04	2.4E+03	1.0	12.21						
high difference from unstable	-0.0143	-5078610	-49	13	-1	0	-12	236.5	272275	-0.0167	537400	-1838000	450000	626000	388000	8	10.46						
low difference from unstable	0.1578	2000	-4	17	15	3	1	0	0	2763	0.6255	3700	6398	2400	15000	2400	1	12.21					
Unstable	high	1.005	5E+06	81	42	32	22	24	197.71	2.125E+03	0.9800	2.6E+03	5138000	1.7E+05	7.4E+04	1.2E+04	1.4	24.48					
	low	0.811	2	23	12	0	0	0	1	0.000E+00	0	0.0E+00	2	0.0E+00	0.0E+00	0.0E+00	0.00	0.00					

Table 7

Summary Properties for the Water-in-Oil States

Property	Stable			Meso			Entrained			Unstable		
	high	low	high	low	high	low	high	low	high	low	high	low
Starting Oil												
Density	0.9674	0.8637	0.977	0.842	0.9907	0.9688	1.005	0.811				
Viscosity (mPa.s)	9583	14	22760	6	59390	2002	5138000	2				
Saturates	65	27	65	28	32	19	81	23				
Aromatics	54	22	39	25	55	29	42	12				
Resins	29	6	30	6	31	15	32	0				
Asphaltenes	19	3	17	3	22	3	22	0				
Waxes	8	4	8	1	12	1	24	0				
Asphaltene-Resin Ratio	1.12	0.4	0.89	0.1	1.11	0.13	1.17	0				
Properties on day of formation												
Appearance	brown solid		brown viscous liquid		black with large droplets		like oil					
Average Ratio of Viscosity Increase	1100		45		13		1					
range	15000		250	2	70	1	8	1				
Average Water Content	80	14	62		42		5					
range	93	65	83	35	62	26	23	1				
Stability*	15000	20	400	1	50	1	60	1				
Properties after one Week												
Appearance	brown solid		broken, 2 or 3 phases		separated oil and water		like oil					
Average Ratio of Viscosity Increase	1500		30		2		1					
range	15000	20	150	1	3	1	2	1				
Average Water Content	79	64	38		15		2					
range	94	64	61	2	35	12	24	0				
Stability*	95000	88	1900	1	434	1	198	1				
Power Law Constants	K	8.596E+05	1.117E+04	1.877E+05	4.376E+02	2.744E+05	2.763E+03	0.000E+00				
n	0.8129	0.0372	0.9765	0.1401	0.9633	0.6255	0.9800	0				
Viscosity (mPa.s)	6.9E+05	2.3E+04	1.7E+05	5.3E+02	5.4E+05	3.7E+03	2.6E+03	0.0E+00				
Complex Modulus (mPa)	4.3E+06	1.0E+05	1.2E+06	10	3.3E+06	6400	5138000	2				
Elasticity Modulus (mPa)	4.3E+06	5.0E+04	1.2E+06	1.6E+03	6.2E+05	2.4E+03	1.7E+05	0.0E+00				
Modulus (mPa)	6.1E+05	2.7E+04	3.3E+05	4.2E+03	7.0E+05	1.5E+04	7.4E+04	0.0E+00				
shear viscosity (mPa.s)	9.0E+04	1.1E+04	5.0E+04	7.0E+02	4.0E+05	2.4E+03	1.2E+04	0.0E+00				
delta (V/E)	1.8	0.11	12	0.24	9.4	1.0	1.4	0.00				
Water- Content (%w/w)	93.79	64.23	61.43	1.89	34.94	12.21	24.48	0.00				

* complex modulus/viscosity of starting oil

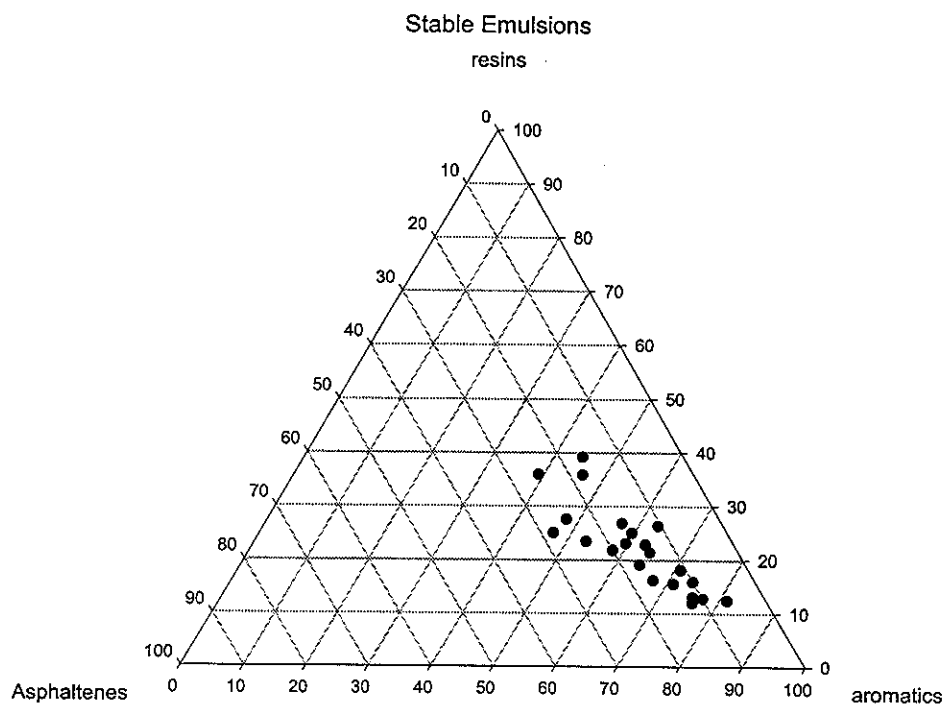


Figure 5 Ternary Diagram of Group Contents
- Stable emulsions

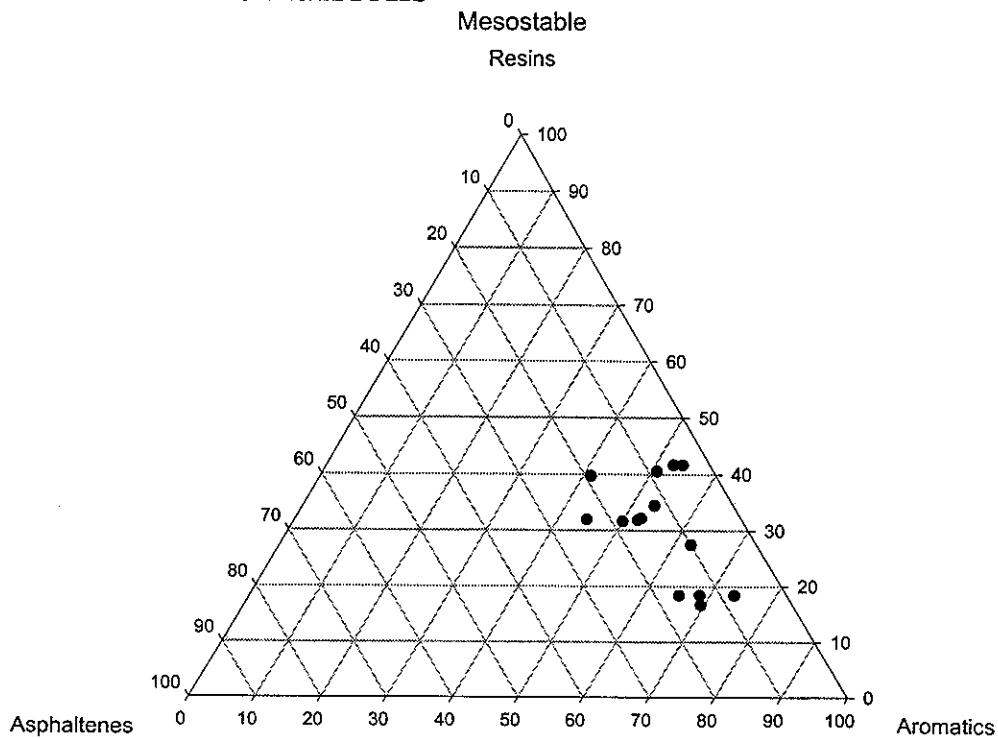


Figure 6 Ternary Diagram of Group Contents
- Meso-stable emulsions

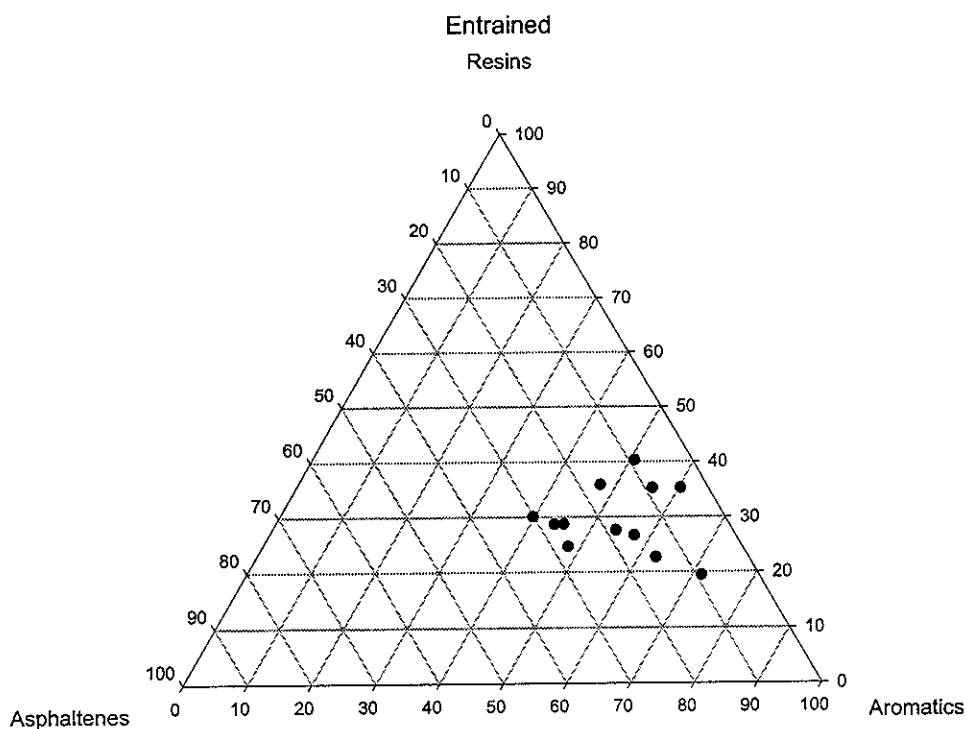


Figure 7 Ternary Diagram of Group Contents
- Entrained Water-in-Oil

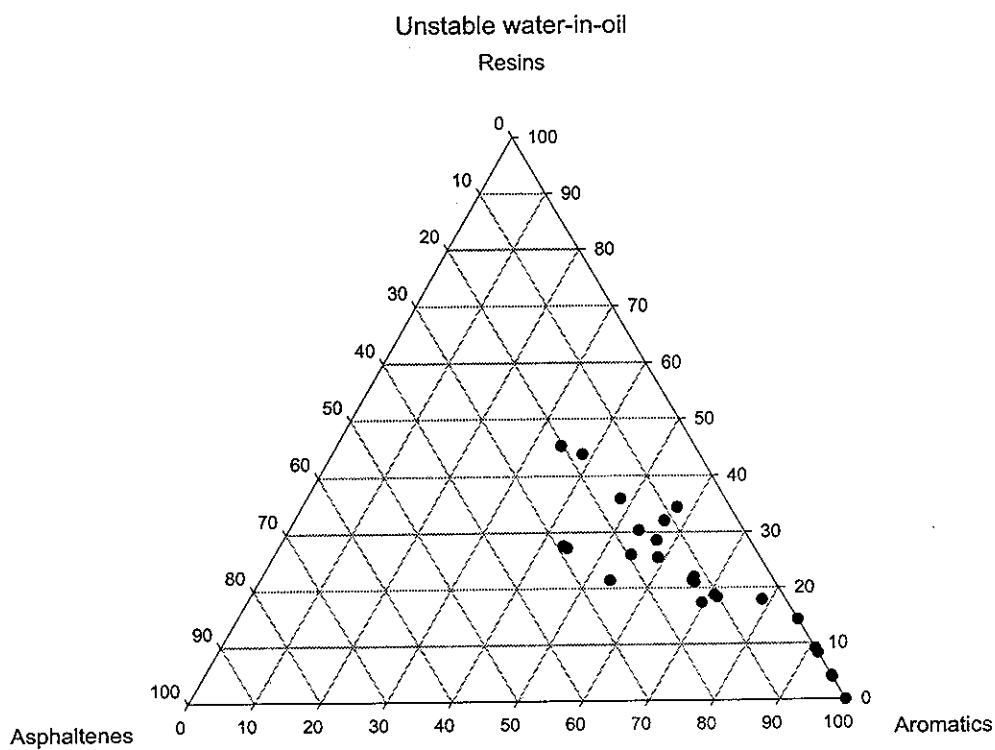


Figure 8 Ternary Diagram of Group Contents
- Unstable emulsions

responsible for the formation of stable emulsions, however, a high asphaltene content can also result in a high viscosity, one that is above the region where stable emulsions form. The asphaltene/resin ratio is generally higher for stable emulsions. In a previous work by the present author, it was shown that the migration rate of asphaltenes in emulsions is very slow (Fingas *et al.* 1996). This indicates that in very viscous oils, the migration of asphaltenes may be too slow to allow for the stabilization of emulsions.

5.0 Conclusions

Four, clearly-defined states of water-in-oil have been shown to be defined by a number of measurements and by their visual appearance, both on the day of formation and one week later. The difference between these states and the oils that form them are summarized in Table 8.

Table 8

Typical Properties for the Water-in-Oil States

		Stable	Meso	Entrained	Unstable
Day of Formation Appearance		brown solid	brown viscous liquid	black with large droplets	like oil
Water Content on first day	%	80	62	42	5
Appearance after one week		brown solid	broken, 2 or 3 phases	separated oil and water	like oil
Water Content after week	%	79	38	15	2
Stable time	days	>30	<3	<0.5	not
Starting Oil					
Density	g/mL	0.85-0.97	0.84-0.98	0.97-0.99	0.8-1.03
Viscosity	(mPa.s)	15-10000	6-23000	2000-60000	2 - 5.1 X 10 ⁶
Saturates	%	25-65	25-65	19-32	23-80
Aromatics	%	20-55	25-40	30-55	5-12
Resins	%	5-30	6-30	15-30	0-32
Asphaltenes	%	3-20	3-17	3-22	0-32
Asphaltenes/Resins		0.74	0.47	0.62	0.45
Properties on day of formation					
Average Ratio of Viscosity Increase		1100	45	13	1
Properties after one Week					
Average Ratio of Viscosity Increase		1500	30	2	1

The results of this study indicate that the formation of both stable and meso-stable emulsions is due to the combination of surface-active forces from resins and asphaltenes and from viscous forces. There exists a range of compositions and viscosities in which each type of water-in-oil state exist. The difference in composition between stable and meso-stable emulsions is small. Stable emulsions have more asphaltenes and less resins and have a narrow viscosity window. Instability results when the oil has a high viscosity (over about 50,000 mPa.s) or a very low viscosity (under about 6 mPa.s) and when the resins and asphaltenes are less than about 3%. Water entrainment occurs rather than emulsion formation when the viscosity is between about 2000 and about 50,000 mPa.s. The formation of stable or meso-stable emulsions may not occur in highly viscous oils because the migration of asphaltenes (and resins) is too slow to permit droplet stabilization.

The role of other components is still unclear at this time. Aromatics dissolve asphaltenes and there is a small correlation observed with the stabilities. Waxes have no role in emulsion formation. Density of the starting oil is highly correlated with viscosity and thus shows a correlation with stability.

The state of the final water-in-oil can be correlated with the single parameter of the complex modulus divided by the starting oil viscosity. This stability parameter also correlates somewhat with the non-Newtonian behaviour of the resulting water-in-oil mixture, with the elasticity of the emulsion and also the water content. These properties are more decisive in defining the state one-week after formation. This is because all states have largely separated into oil and water except for stable emulsions. The water content retained one-week after the formation process is a very clear discriminator of state.

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